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Thermodesorption coupled to GC–MS to characterize volatiles formation kinetic during wood thermodegradation

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ABSTRACT

Identification of volatile degradation products generated and released during wood mild pyrolysis is important to better understand thermodegradation mechanisms. Previous studies have shown that thermodesorption coupled to GC–MS is an attractive tool to characterize and quantify products formed during wood thermal treatment indicating higher susceptibility of hardwoods to thermodegradation compare to softwoods. The aim of this study is to elucidate wood thermodegradation pathways with special emphasis on the kinetics reactions. To achieve this objective, one hardwood species (beech) and one softwood species (Silver fir) were subjected to thermal treatment directly in the thermal desorption glass tube of thermodesorber connected to GC–MS using helium as carrier and at temperatures of 210 and 230 °C for different times ranging from 10 to 80 min. The volatiles compounds formed were analyzed by gas chromatography coupled to mass spectroscopy. From GC–MS data collected in this study, the kinetic curves of the formation of some of the products as a function of thermal treatment duration were established. Assuming that acetic acid and furfural were formed from hemicelluloses and vanillin from lignin, Arrhenius equation was used to estimate the mean activation energy formation of these two degradation by-products allowing obtaining indirect information on the thermal stability of both polymer.

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1. Introduction

Wood heat treatment by mild pyrolysis is used to improve wood properties such as its decay durability and dimensional stability [1,2]. These new properties are the result of chemical and physical modifications of wood cell wall polymers during thermal treatments [3–5]. Therefore, the knowledge of the mechanisms schemes of the wood thermo-degradation is of great interest to unravel important parameters that will fit in a kinetic model, usable and applicable to the industrial/commercial wood heat treatment process, and help in drafting recommendations concerning the operating temperature, residence time to improve and control the properties of thermally treated wood.

Previous studies have shown that thermodesorption coupled to GC–MS is a robust and reliable method for identification and quantification of volatile degradation products formed during wood mild pyrolysis [6]. This method can therefore be used to yield valuable information on mechanisms of wood thermodegradation and to understand the differences in kinetics between thermally treated softwood and hardwood species [7,8]. The higher susceptibility of hardwoods to thermodegradation compared to softwoods has been attributed to their higher content in acetyl groups from acetylated glucoroxylan leading to the formation of considerable amount of acetic acid involved in hemicelluloses and lignin degradation. Even if softwoods and hardwoods present different chemical compositions, similar degradation products have been identified during mild pyrolysis excepted for degradation products resulting from syringyl units. The main difference in the thermo-degradation kinetics was related to the thermal treatment temperature levels and the amount of acetic acid released during thermal treatment. Thermal degradation of softwoods occurred in the temperature range of 210–230 °C. Slightly lower temperatures are necessary for hardwood species. The majority of kinetic methods used in the area of thermal analysis to determine the rate of degradation of wood consider two variables, the temperature and the extent of conversion. The extent of conversion is determined as a fraction of the total mass loss in the thermodegradation process involving numerous reactions. Thermal analysis methods are therefore not species specific and cannot be directly linked to specific reactions of molecules. Consequently, experimental parameters are generally "global parameters" corresponding to the contribution of numerous intrinsic kinetic parameters of the different individual reactions. Contrary to these methods, the use of thermodesorption coupled to GC–MS allowed the identification and quantification of

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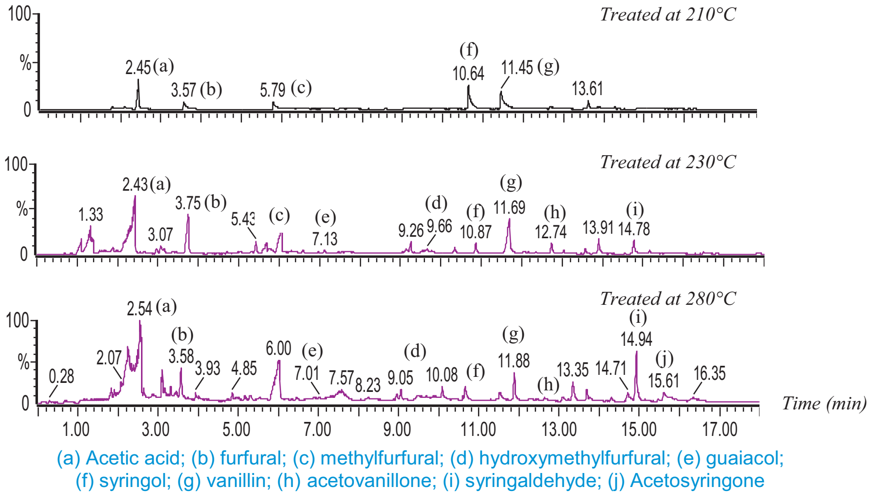

Fig. 1. Chromatograms of degradation products identified by TD-GC–MS from beech sawdust treated at 210, 230 and 280 °C during 15 min under helium.

volatile degradation products formed during wood thermodegardation allowing to obtain indirect information on the stability of the polymers from which these products are formed.

The aim of this work is to use thermodesorption coupled to GC–MS to study the kinetics of formation of acetic acid, furfural and vanillin chosen as representative molecules of hemicelluloses and lignin degradation. Identification by comparison with the mass spectra of reference compounds and integration of the peak are used to generate concentration–time curves of each product. Assuming the fact that global kinetic parameters are functions of the intrinsic kinetic parameters of the different individual reactions leading to the formation of each of these products, these informations are used to estimate the constant rate and the energy of activation allowing obtaining indirect informations on the thermal stability of hemicelluloses and lignin.

2. Experimental methods

2.1. Material

One hardwood species (beech, *Fagus sylvatica L.*) and one softwood species (Silver fir, *Abies pectinata*) were selected for this study. Defect free air dried wood chips of each species were grounded to fine sawdust. Only fractions of sawdust that passed 0.5 mm and retained by 0.2 mm sieves were retained for further testing. The accepted fractions were dried at 103 °C for 24 h to remove all the water and then stored in closed bottle before analysis.

2.2. Thermodesorption-GC–MS

Approximatively 30–40 mg of dried sawdust was placed in a glass thermal desorption tube with ¼ in. outer diameter and 3.5 in. long from Supelco, Inc. and end capped with glass wool. Thermal treatment was performed in a Turbomatrix 300 Thermal Desorber system from Perkin Elmer, USA. The conditions included a pre-purge for 1 min at room temperature using helium carrier gas at 1 mL min^{-1} followed by heating at 210, 230 and 280 °C for different durations in the glass thermal desorption tube of the thermodesorber using carrier gas at 20 mL min^{-1} and splitless trapping at −30 °C. The trap was desorbed at 300 °C at 1 mL min^{-1} through a transfer line at 300 °C with a split flow of 40 mL min^{-1}. The volatile wood degradation products were analyzed by GC–MS after thermodesorption. GC–MS analysis was performed on a Clarus 500 GC gas chromatograph (Perkin-Elmer) equipped with a 5%

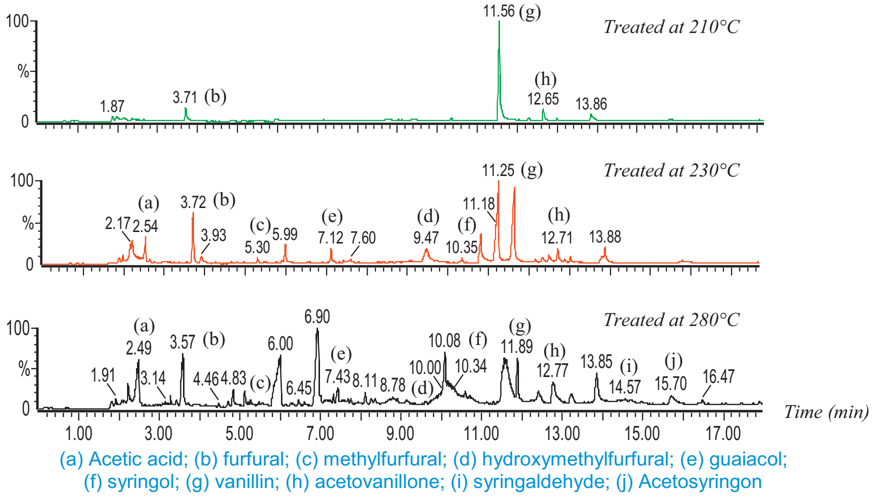

Fig. 2. Chromatograms of degradation products identified by TD-GC–MS from Silver Fir sawdust treated at 210, 230 and 280 °C during 15 min under helium.

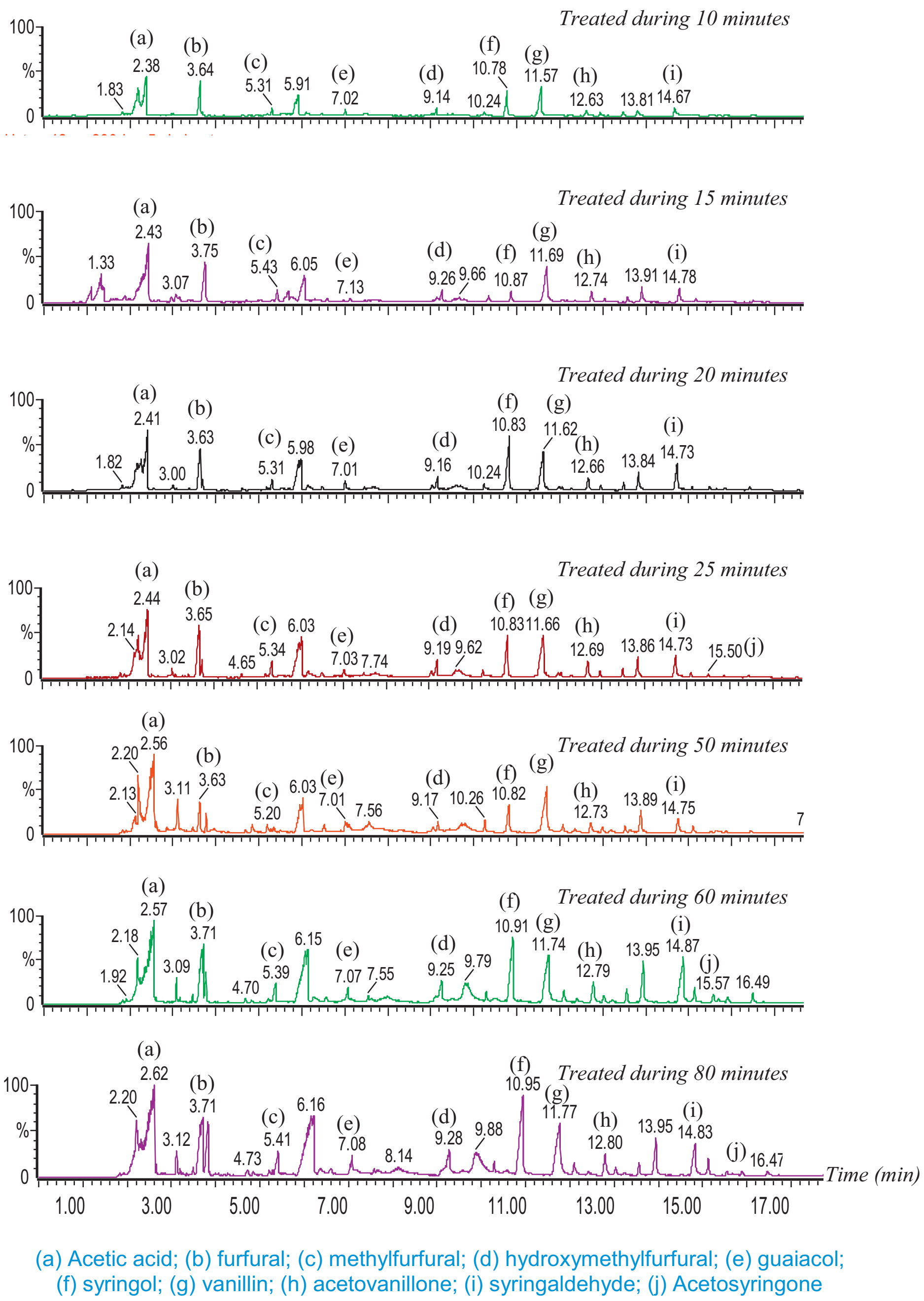

Fig. 3. Chromatograms of degradation products identified by TD-GC–MS from beech sawdust treated at 230 °C under helium for different durations.

diphenyl/95% dimethyl polysiloxane fused-silica capillary column (J&W Scientific DB-5, 30 m × 0.25 mm × 0.25 μm) and controlled by Turbomass (v5.4.2) software. Ionization was achieved under the electron impact method (70 eV ionization energy). The components were identified on the basis of comparison of their mass spectrum with the NIST Library 2005 through the NIST MS Search 2.0. Identification was considered as relevant for the match and reverse match coefficient values above 900.

Quantification of degradation products was expressed in peak absolute area unit per mg of sawdust used for TD-GC–MS analysis. Maximum relative standard deviation calculated from 3 replicates for given curing conditions was estimated to ±5%. Absolute area per mg of sawdust of a given product “A” was then used to determinate the relative concentration of product “A” and plot the relative concentration of “A” versus time allowing determination of the kinetic parameters such as the rate constant and the energy of activation.

Due to the complex nature of the chemical composition of wood and to the complexity of wood thermo-degradation pathways, global kinetic models were investigated to describe the formation of acetic acid, furfural and vanillin resulting from wood degradation.

Indeed, wood pyrolysis involves a complex set of sequential and parallel unimolecular and bimolecular reactions that are often impossible to characterize at any significant level of detail. Consequently, kinetic model used to describe such types of reactions are generally global kinetic approach [9–15]. Such approach assumes that the true reaction system is too complex to be characterized in any fundamental way, so that the reaction is described in terms of pseudo species, which are themselves complex materials or

Table 1
Evolution of the relative concentrations of acetic acid, furfural and vanillin formed during thermal treatment at different temperatures for different durations.

Wood species	Product	Temperature (°C)	Treatment duration (min)							
			0	10	15	20	25	50	60	80
Silver fir	Acetic acid	210	0	0.3	0.2	0.4	0.5	0.5	0.6	0.8
	Vanillin	210	0	0.6	0.9	0.8	0.9	1.3	1.4	1.4
	Furfural	210	0	0.03	0.04	0.05	0.1	0.16	0.2	0.24
	Acetic acid	230	0	1.7	1.6	2.8	4.2	4.6	5.0	6.5
	Vanillin	230	0	3.0	2.6	3.2	4.2	5.3	5.9	6.0
	Furfural	230	0	0.65	0.92	1.26	1.36	1.67	1.72	2.11
	Acetic acid	280	0	14.1	16.0	16.1	17.1	18.4	18.5	18.6
	Vanillin	280	0	24.6	29.2	30.5	28.1	38.6	39.5	40.4
	Furfural	280	0	7.3	7.8	8.6	8.7	9.2	9.7	10.0
Beech	Acetic acid	210	0	0.9	1.0	1.1	1.6	2.1	2.4	3.7
	Vanillin	210	0	1.3	1.4	1.6	2.0	3.2	3.2	3.2
	Furfural	210	0	0.21	0.31	0.36	0.48	1.06	1.05	1.06
	Acetic acid	230	0	8.7	9.7	12.9	13.7	17.2	24.6	30.0
	Vanillin	230	0	2.97	4	5	5.4	6.82	7.99	8.19
	Furfural	230	0	2.3	3.0	3.4	4.3	5.8	5.9	6.4
	Acetic acid	280	0	73.5	76.5	76.6	86.8	84.1	88.7	100.0
	Vanillin	280	0	7.9	8.2	10.1	11.7	13.1	12.9	13.2
	Furfural	280	0	3.6	4.5	6.1	6.5	6.6	6.7	6.9

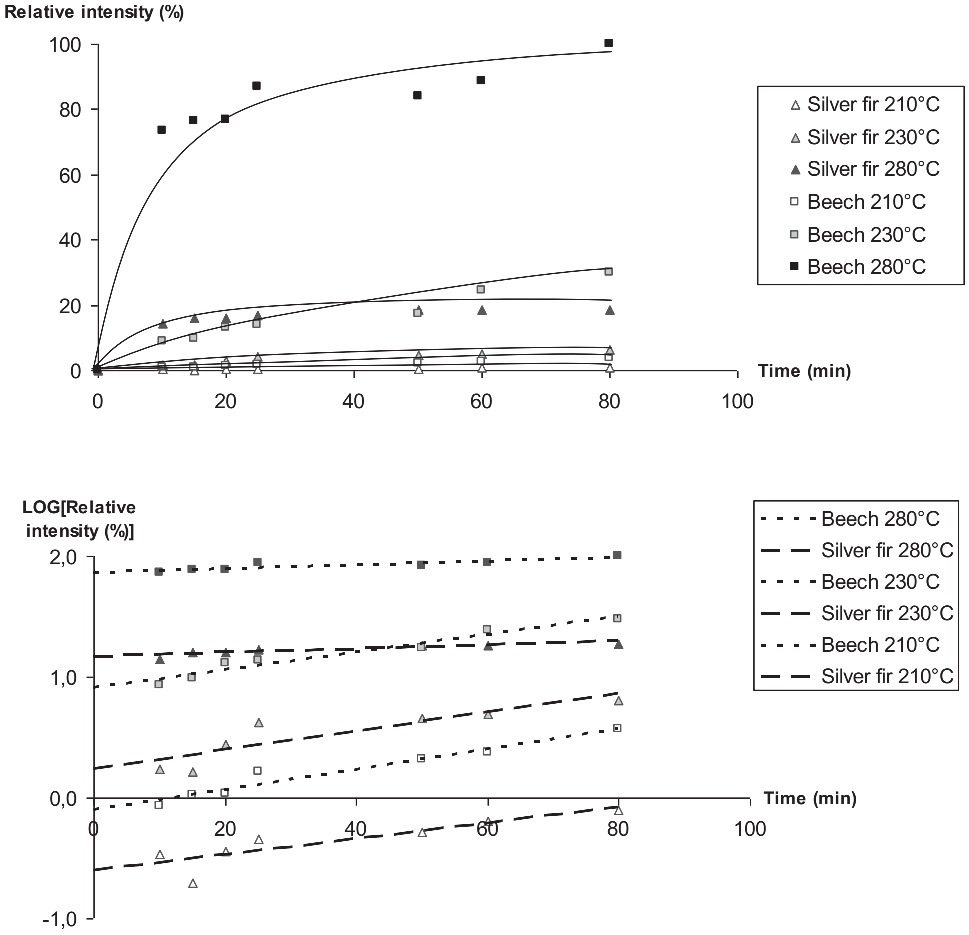

Fig. 4. Formation and determination of rate constants of acetic acid formation at 210, 230 and 280 °C from beech and Silver fir.

mixtures. Absolute concentration is not important, as all species are characterized in terms of the fraction of their initial or final value. Even if a variety of global kinetic models existed, including first-order, *n*th-order, nucleation and sequential models as well as models having Gaussian, Weibull, and discrete activation-energy distributions [16], we have chosen to use the most simplified approach using a first order Arrhenius equation describing the formation of the different volatile products formed from wood thermodegradation.

3. Results and discussion

Figs. 1–3 present as an example the chromatograms obtained at 210, 230 and 280 °C for both wood species and at 230 °C for all

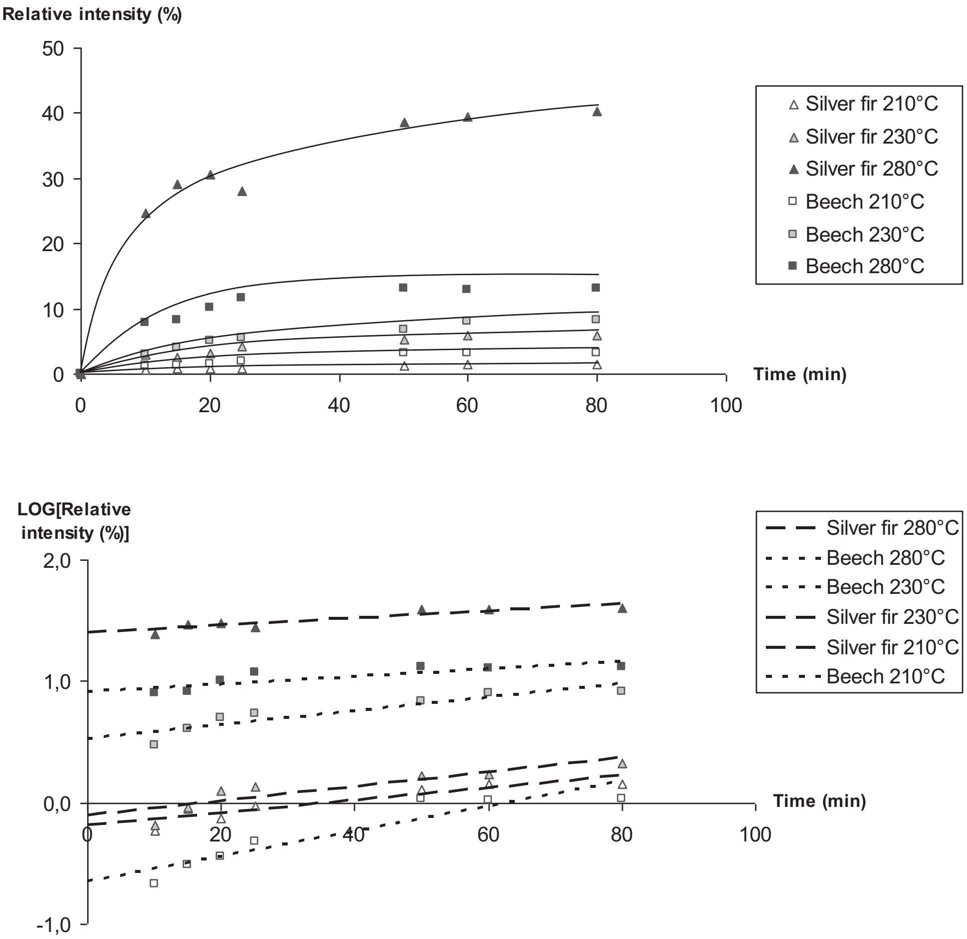

Fig. 5. Formation and determination of rate constants of vanillin formation at 210, 230 and 280 °C from beech and Silver fir.

treatment durations for beech. It is obvious from these data, that degradation of wood components is slower at low temperature and increases as the temperature increases confirming previous investigations [6]. For a given temperature, the quantity of each degradation product increases progressively as the treatment duration increases. The main degradation products identified were acetic acid, furfural, methylfurfural, hydroxymethylfurfural resulting from hemicelluloses thermal degradation, guaiacol, syringol, vanillin, acetovanillone, syringaldehyde and acetosyringone resulting from lignin degradation.

The rate of the modification of the concentration of one or more components in function of time known as the kinetics of a reaction is a concept well established and used to characterize the rate of a chemical reaction. This concept will be used in this work to characterize the modification/transformation of a measurable compound or series of compounds produced/generated during the thermal treatment of wood. Acetic acid, furfural and vanillin will be used as representative thermo-degradation products of hemicelluloses and lignin, respectively. Assuming to simplify the model a first order reaction describing global kinetic approach during which both products are produced, the production of acid acetic, furfural or vanillin in terms of quantity in function of treatment duration and temperature can be determined according to the formula:

$$v = k[A] \tag{1}$$

where k is the rate constant of the reaction and $[A]$ the concentration of compound A.

The rate constant of the reaction k is a constant for a first order reaction and can be obtained by plotting the variation of the concentration of A in function of time. Logarithmic transformation of the concentration is often used to facilitate the calculation of k.

Table 2
Determination of kinetic parameter of acetic acid, furfural and vanillin formation.

		Rate constant (min^{-1})			Activation energy (kJ mol^{-1})		
		k_1 T_1 = 210 °C	k_2 T_2 = 230 °C	k_3 T_3 = 280 °C	$E_{aT_1-T_2}$	$E_{aT_2-T_3}$	$E_{aT_1-T_3}$
Silver Fir	Acetic acid	0.0278	0.1313	0.2652	156.9	32.5	71.6
	Vanillin	0.0494	0.1765	0.2865	128.7	22.4	55.8
	Furfural	0.0031	0.0223	0.0795	199.4	58.8	103.0
Beech	Acetic acid	0.241	1.1285	1.7998	156.0	21.6	63.8
	Vanillin	0.2197	0.2988	0.3741	31.1	10.4	16.9
	Furfural	0.0148	0.0637	0.0975	147.5	19.7	59.8

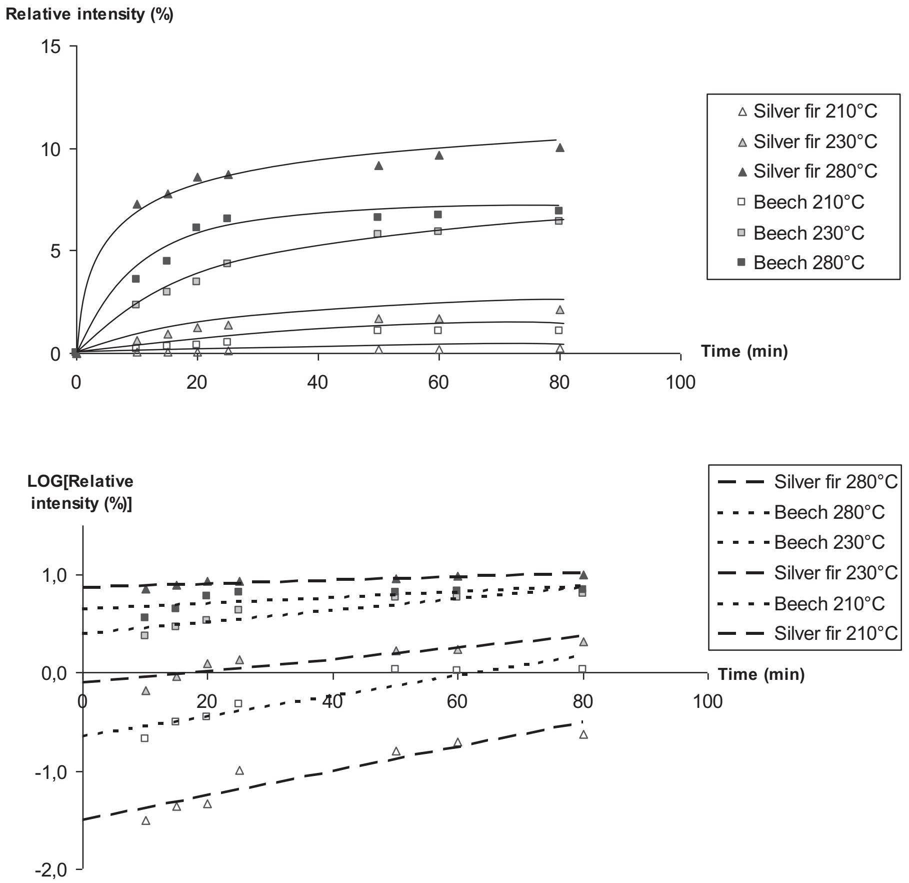

Fig. 6. Formation and determination of rate constants of furfural formation at 210, 230 and 280 °C from beech and Silver fir.

According to Arrhenius equation, the rate constant is given by the following formula:

$$k = A \cdot e^{-E_a/RT} \tag{2}$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature in Kelvin.

The determination of the activation energy as defined in Eq. (2) can be achieved if the rate constants k_1 and k_2 are known at minimum two different temperatures T_1 and T_2.

$$k_1 = A \cdot e^{-E_a/RT_1} \text{ and } \quad K_2 = A \cdot e^{-E_a/RT_2} \tag{3}$$

It is then possible to use Eqs. (3)–(6) to estimate the energy of activation of a compound.

$$\frac{k_1}{k_2} = e^{-E_a/RT_1} \times e^{-E_a/RT_2} = e^{E_a/RT_2 - E_a/RT_1} \tag{4}$$

$$\text{In}\frac{k_1}{k_2} = \frac{E_a}{RT_2} = \frac{E_a}{RT_1} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{E_a}{R} \times \frac{T_1 - T_2}{T_1 \cdot T_2} \tag{5}$$

$$E_a = R \times \frac{T_1 \cdot T_2}{T_1 - T_2} \cdot \text{In}\frac{k_1}{k_2} \tag{6}$$

Table 1 reports the relative concentrations of acetic acid, furfural and vanillin as a function of treatment duration based on the integration of the peaks areas. For comparison purpose, peaks have been normalized on the basis of the peak of acetic acid formed during beech heat treatment at 280 °C after 80 min, which present the higher intensity and for which an arbitrary value of 100 was attributed.

Assuming global kinetic parameters and first order reactions for the formation of acetic acid and vanillin, it is possible to determine from the slopes of the relative intensity–time curves measured at two different temperatures their activation energies allowing an indirect evaluation of the thermal stability/degradation of hemicelluloses and lignin. Figs. 4–6 represent the relative intensity–time curve of acetic acid, furfural and vanillin formation at 210, 230 and 280 °C for both wood species used in this study.

The quantities of degradation products are considerable higher for higher temperature treatment. It was also noticeable that the amount of acetic acid generate by softwood was always lower compare to hardwoods. Generation of acetic acid is strongly dependent of the nature of wood species, beech leading to higher amounts of acid compared to silver fir. This may be related to the nature of hemicelluloses present initially in hardwood and softwood species [17,18].

Determination of rate constants and calculation of activation energies for acetic acid, furfural and vanillin formation are reported in Table 2. According to ICTAC Kinetics Committee recommendations, three different temperatures were investigated to determine the Arrhenius temperature dependence and the accuracy of the kinetic parameters thus obtained [19].

Results obtained clearly indicated that thermal degradation is faster for beech than for Silver fir confirming previous investigations indicating the higher susceptibility of hardwoods to thermo-degradation comparatively to softwoods [7,8]. Activation energies calculated for a given compound using two given experimental temperatures are always lower in the case of beech comparatively to Silver fir. However, the results indicated a strong disparity of the value of calculated activation energies according to the range of temperature used indicating clearly a non Arrhenius dependence. Indeed, activation energies calculated with the two lower temperatures are always higher than those calculated with the two higher temperatures, while activation energiescalculated with the lower and higher temperatures gave intermediate results. These results clearly highlighted the complexity of reaction involved in wood thermo-degradation and the importance of catalytic effect of degradation products like acetic acid. Indeed, if we consider different compounds or mechanisms leading to a similar product, it should expected that reactions involving lower activation energies take place at lower temperatures comparatively to reactions involving higher transition states, which should take place at higher temperature. The fact that average mean activation energy decreases with the treatment intensity is due to external parameters like different organic acids released during treatment catalyzing depolymerization of wood's polymers. In all cases, lignin seems more susceptible to degradation as demonstrated by the lower activation energies calculated for vanillin formation comparatively to acetic acid or furfural formation. It has been proposed in the literature that thermal treatment is a series of complex reactions of decomposition of wood main constituents in the proportion to their content [12] with lignin decomposing into char and volatiles, cellulose into tar, char and volatiles [20]. According to Di Blasi [21,22], the activation energies of the degradation/devolatilization process vary roughly between 60 and 170 $\mathrm{kJ\,mol^{-1}}$ while, when higher temperatures are examined lower values comprised between 56 and 89 $\mathrm{kJ\,mol^{-1}}$) were obtained due to the presence of strong heat/mass transfer interferences. Results obtained in our study indicated quite similar behaviour showing a decrease of the E_a values as the temperature increases. This can be the result of the highly different reaction mechanisms and kinetic constants involved in the multi-step degradation kinetics of wood under isothermal conditions leading to different global degradation mechanism according to the range of temperatures studied. Even if wood degradation results from complex decomposition pathways, it appears that utilization of kinetic curves obtained using thermodesorption coupled to GC–MS afford valuable data to estimate mean activation energies of a given degradation product resulting from a global kinetic approach allowing to obtain indirect information on the stability of the different wood macromolecules according to the species. Even if it remains difficult to calculate true activation energies, this method may find valuable applications for comparison purposes to estimate stability of different wood species.

4. Conclusion

Utilization of TD-GC–MS under isothermal conditions for different treatment times allows determination of kinetic of wood thermodegradation products formation. According to Arrhenius equation and using peak intensity–time plots recorded at different temperatures for a given degradation products, it was possible to determine their mean activation energy formation assuming global kinetic parameters.

Applied to acetic acid, furfural and vanillin, it was possible to show that activation energies measured in the case of beech are lower for all products comparatively to those measured in the case of Silver fir. Activation energy of vanillin is in all cases lower indicating the higher susceptibility of lignin to thermodegradation compared to hemicelluloses on the basis of the different degradation products considered. The strong disparity of the values of activation energies estimated according to different range of temperatures indicated clearly a non Arrhenius dependence. The systematic decrease of all value of activation energy as the temperature increases indicated important catalytic effect of released degradation products catalyzing further degradation reactions. Even if it seems difficult to determine exact values of activation energy, TD-GC–MS permits comparison of the relative stability of the different wood polymers according to their degradation products and appear therefore as an attractive complementary method to classical thermogravimetric methods to study wood thermodegradation allowing determination of kinetic parameters in relation with volatiles products formation.

Acknowledgments

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